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16. ABSTRACT

The vapor pressure and solubility (as subcooled liquids) and Henry's Law constants (HLCs) for the individual chlorobiphenyl compounds (CBC) in Aroclor 1242, 1254, and 1260, as well as the HLCs for toxaphene, have been determined with an equilibrium technique. The results were obtained from one set of measurements, for all of the CBC present in the materials of interest, the subcooled organic mixtures that are partitioning in the environment. The HLCs of the CBC varied from about 3.3×10^{-4} to 5×10^{-5} atm·m^3/mol at 20° C, and those of the Aroclors were about were about 2×10^{-4} atm·m^3/mol. These HLCs are such that the transport rate of these compounds through the air/water interface should be dependent on both the gas- and liquid-phase mass-transfer coefficients. The solubility of the polychlorinated biphenyls (PCBs) in water is shown to be significantly lower when a solution is prepared by adding an organic solution (acetone, methanol, etc.) of the PCBs to water. These results affect the design and the interpretation of the results from toxicity experiments.

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JOURNAL ARTICLE

Equilibration of Polychlorinated Biphenyls and Toxaphene with Air and Water

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■ The vapor pressure and solubility (as subcooled liquids) and Henry's law constants (HLCs) for the individual chlorobiphenyl compounds (CBC) in Aroclor 1242, 1254, and 1260, as well as the HLCs for toxaphene, have been determined with an equilibration technique. The results were obtained from one set of measurements, for all of the CBC present in the materials of interest, the subcooled organic mixtures that are partitioning in the environment. The HLCs of the CBC varied from about 3.3×10^{-4} to 5×10^{-6} atm·m^3/mol at 20 °C, and those of the Aroclors were about 2×10^{-4} atm·m^3/mol. These HLCs are such that the transport rate of these compounds through the air/water interface should be dependent on both the gas- and liquid-phase mass-transfer coefficients. The solubility of the polychlorinated biphenyls (PCBs) in water is shown to be significantly lower when a solution is prepared by adding an organic solution (acetone, methanol, etc.) of the PCBs to water. These results affect the design and the interpretation of the results from toxicity experiments.

Introduction

Polychlorinated biphenyls (PCBs) and toxaphene are each mixtures of a large number of individual compounds that are widely distributed in the environment. Their transport through the environment, while reasonably well understood, is quite complex and has not yet been quantified. The transport is controlled by the solubility, vapor pressure, and mass-transfer coefficients of the individual compounds in the mixtures. The major problem when this project was undertaken was that the values of these properties, and their range, either are not known or are not known with sufficient accuracy (*1–3*). Without this information, good calculations of the fugacities of these compounds in different phases, and the direction and magnitude of the transport between phases, which is crucial for for an understanding of their environmental chemistry, cannot be made.

Two different approaches have been taken to determine the physical properties of the Aroclor mixtures. The first is to make measurements on individual chlorobiphenyl compounds (CBC) and then to sum and extrapolate the results to the mixtures. The second approach is to make direct measurements on the commercial mixtures, the Aroclors and on mixtures found in the environment.

The advantage of working with the individual compounds is that they can be obtained quite pure and measurements can be made more rapidly, accurately, and precisely. In recent years a number of studies on the solubility (*4–6*), vapor pressure (*7–10*), and Henry's law constant (HLC) (*11–13*) of individual CBC have been reported.

There are two disadvantages of this approach. The first is that measurements have to be made on a large number of individual compounds. The second is that the individual CB and chlorocamphene compounds are only laboratory curiosities and are mostly solids but they occur in the environment only as mixtures of subcooled liquids. Corrections to the values measured on the solids then have to be made. These corrections can be greater than a factor of 30 for solubilities. The assumptions and errors introduced in making the corrections decrease the accuracy of the final results.

The advantages of making the measurements on the mixtures are that one measurement gives the desired information on all of the CBC present and that you are making the measurements on the material of interest, the mixtures. If the properties of the individual components

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are altered by being in the mixture, this will be reflected in the results. The disadvantages have been the lack of an analytical method for quantifying each of the components of these mixtures. A few studies using this approach have been reported (*12*, *14*).

The introduction of capillary gas chromatography, on-column injection, and high-efficiency columns made the separation of all of the CBC present in PCB mixtures practical. At that time we undertook a project to determine the HLCs for all the CBC that occur in the Aroclors.

Initially, the individual response factors for most of the CBC were not known, so that, while the individual compounds could be separated and their relative peak areas determined, the amounts could not be quantified. Such information is sufficient to permit the HLCs to be determined for the individual CBC, and we began a project to accomplish this. Fortunately, after the project was begun the response factors for each of the 209 CBC became available (*15*). These response factors than permitted with solubility and vapor pressure of each compound to be determined with the Aroclor mixtures as the source of the compounds.

Two different approaches have been used to determine HLCs for chlorinated biphenyl compounds and air/water partition coefficients for the Aroclor mixtures. One is a kinetic method based on the rate of loss of a compound from water solution by stripping with a gas (*1*, *11*, *16*). The other is a thermodynamic method where the air and water concentrations of a compound are determined under equilibrium conditions and the HLC is calculated as their ratio (*12*, *13*, *17*, *18*). Burkhart et al. (*13*) have recently discussed the validity and limitations of this approach.

It would be useful to have measurements at different temperatures to permit transport calculations to be made for the different seasons and also to permit the temperature variation in the physical properties of the PCBs to be evaluated. This is a report of those determinations and the results.

Methods and Procedures

The method used was one based on thermodynamics. It depended on the fact that after equilibrium has been reached in a closed system the fugacity of any material is the same in each of the phases present (*19*, *20*). Thus, each of the phases present in a closed container containing air, water, and an excess of a Aroclor mixture would be saturated with each of the individual CBC with respect to the starting mixture. Experiments were set up in a contant-temperature chamber by adding a large excess of one of the Aroclor mixtures to a 4-L glass bottle partially filled with water. The water was stirred for 2 weeks and then left stand undisturbed. After equilibrium between all of the phases present (PCB, water, vapor, glass adsorbed, surface layer; etc.) was attained, the concentration and composition of the CBC in the air and water phases were determined. This information, along with the mole fraction of each compound in the starting mixture, permitted the solubility, vapor pressure, and HLC of each of the component CBC (as subcooled liquids) to be calculated (*14*, *16*, *18*, *21*).

There were a number of difficulties and complications: even when saturated, air and water contain only small total amounts of these chlorinated compounds; all materials (including metals and Teflon) absorb significant amounts of these compounds compared to the amounts being measured; it takes weeks for equilibrium between the liquid mixtures and water to become established; a surface layer of undissolved compounds is normally present on the water.

The details of the experimental procedures will be described for Aroclor 1254. The identical procedure, with the exception of the volume of vapor sampled, was followed for Aroclors 1242 and 1260 and toxaphene. The Aroclor samples used were obtained from the Food and Drug Administration (FDA). They were from lots that had been characterized for packed-column gas chromatography (GC) quantification by Sawyer (*22*). The toxaphene (6740, lot C697) was from the U.S. EPA's Pesticides and Industrial Chemical Repository Laborstory.

Aroclor 1254 (170 mg) was added to 750 mL of clean water (deionized, refluxed for 24 h with acid permaganate, distilled from glass through a packed column, and the first 10% and last 30% of the distillate discarded) in a clean, 4-L glass bottle. A Teflon-coated stirring bar was added, and the bottle was covered with a piece of aluminum foil, capped, placed in a constant-temperature room (19.5 ± 0.6 °C), and stirred until the composition in the water phase became constant. The solutions were allowed to stand undisturbed for several weeks until the measured dissolved concentrations became constant. The concentrations measured were similar to those reported in the literature (*14*, *23*).

Water samples were collected by inserting a clean 10-mL graduated pipet through the aluminum foil and into the water, taking care to avoid obvious PCB droplets on the water surface. Six milliliters of water was drawn into the pipet and, with the pipet remaining in the water, allowed to equilibrate with the pipet for several minutes. Then an additional 6 mL was drawn into the pipet, the pipet was withdrawn from the bottle, the external surface was wiped with a tissue, 1 mL was expelled from the pipet and discarded, and 3 mL was drained into a tared vial containing a weighed amount (~0.3 g) of hexane. the vial was weighed to determine the sample amount and shaken to extract the PCBs into the hexane. The hexane extract was then analyzed by GC.

The major problem with collecting the water samples was in avoiding the incorporation of undissolved PCBs present on the water surface into the sample. Their presence, however, was easily detected by comparing the ratio of the peak heights of late-eluting peaks with those of the early peaks. In the starting mixture, the ratio of the height of the last major peak to the tallest peak in the chromatogram was 0.8. In the water samples this ratio was only 0.07 due to the lower solubility of the higher molecular weight, late-eluting peaks. Thus, a water sample containing 5% contamination with surface layer material (undissolved PCBs) would have a 57% increase in the peak height of the last major eluting peak. A 20% change in peak height of the last major peak could be readily detected, resulting in a limit of detection for surface contamination of about 2%.

There was no observable change in the composition of the saturated Aroclor solutions over a period of more than 1 year. The composition of the toxaphene solutions, however, showed significant changes with time. These changes began while the solution was being saturated and continued for the duration of the sampling period, about 1 month. Much of this change is presumably due to the solvolysis of some of the specific chlorocamphene compounds present. These changes are probably also related to the differences observed in the toxaphene found in the environment, "weathered", as compared to virgin toxaphene (*24*).

Collection tubes for the vapor samples were prepared by placing about 0.5 g of Florisil (60–100 mesh, activated at 600 °C, stored at 130 °C) between glass wool plugs in

a 7 mm diameter glass disposable pipet. One end of the collection tube was connected with tubing to the top of a large separatory funnel containing water. The other end of the collection tube was inserted into the bottle containing the saturated vapor through the foil cover. By draining a measured volume of water from the separatory funnel, a known volume of the saturated vapor was drawn through the Florisil in the pipet. The compounds on the Florisil were recovered by eluting the collection tube with hexane. With this method, compounds in the vapor samples are exposed to a minimum of new surface, and this surface is all rinsed by the hexane used to elute them from the Florisil, minimizing the loss of sample.

While the saturated air in the bottle was being withdrawn for vapor collection, air was being drawn into the bottle and diluting the vapor remaining. Since a significant proportion (10–40%) of the vapor in the bottles was withdrawn with many of the samples, a correction for this dilution was required. In order to correct the volume of the sample collected for the dilution that occurred, it was assumed that the air drawn into the bottle mixed completely and uniformly with the vapor present. Also, it was demonstrated that the rate of saturation of the vapor was slow compared to the sample withdrawal rate. The following equilibrium dilution formula was used to correct for the dilution of the vapor sample:

$$V_c = V_b(1 - e^{-V_s/V_b})$$

where V_c is the corrected sample volume, V_b is the vapor space in the bottle, and V_s is the total volume of sample collected.

Separation of the individual compounds present in the samples was by gas chromatography (GC), and a ^{63}Ni electron-capture detector (ECD) was used for quantification. The capillary column used was a 50-m, SE-54 fused-silica column, temperature programmed from 100 to 240 °C at 4 deg/min. Identification and quantification were by comparison with injections of standard solutions of the pure individual compounds (*15*). The Aroclor 1242 vapor and liquid samples and the toxaphene samples were run by different laboratories. The same type of GC columns and the same chromatographic conditions were used. Packed-column GC used a 2 m × 2 mm column coated with OV-101 (chemically equivalent to the SE-54). Individual runs were programmed from 182 to 210 °C at 3 deg/min. Quantification was by the method of Webb and McCall (*25*) with the standards and compositions of Sawyer (*22*).

After the measurements at 19.5 °C were made, the room was cooled to 4 °C, and samples were again collected after the solutions came into equilibrium at the lower temperature.

Calculations

The results from capillary GC analyses were corrected for the initial sample size, dilutions, and the instrument response to yield the concentration of each compound in the saturated water (mol/m^3) or vapor (atm) phases. The HLC (atm·m^3/mol) for the CBC was calculated from the ratio of the measured vapor pressure of each compound to its measured solubility in water at equilibrium (*17*). An estimate of the HLC for toxaphene was obtained by determining the ratio of the area of the GC chromatograms for the vapor and water samples [(area of toxaphene per cubic meter of air/area of toxaphene per cubic meter of water) × RT]. This is equivalent to assuming that equal percentages of moles of chlorocamphene compounds in both phases and the standard had the same response factors.

The mole fraction of each compound in the Aroclor mixtures was determined by dividing the moles of each compound present in a given weight of the mixture by the total moles of all of the compounds present. The vapor pressure (P°_L) and solubility (S°_L) of each of the pure CBC (as subcooled liquids) was calculated by dividing the observed concentration in the saturated air (p) or water phase (s) by the mole fraction (x) of that compound in the Aroclor (FDA) used to saturate the air and water:

$$P^\circ_L = p/x \quad (1)$$

$$S^\circ_L = s/x \quad (2)$$

This assumes that the behavior of the CBC in the Aroclor mixtures is ideal (*14*, *21*, *26*).

The solubilities, vapor pressures, and HLCs for those compounds that were present in more than one Aroclor at quantifiable levels were calculated by using a weighted average of the result from each determination. The results were weighted by the mole fraction of the compound in each of the Aroclors. For instance, Aroclor 1254 consisted of 6.1% of compound 153, and it yielded a calculated solubility of 11 μg/L. Aroclor 1260 consisted of 11.4% of this compound, and it gave a calculated solubility of 8 μg/L. Thus, the solubility of compound 153 (S°_{153}) reported in Table I is 9.14 μg/L:

$$S^\circ_{153} = \frac{(11 \times 6.1) + (8 \times 11.4)}{6.1 + 11.4} = 9.14\ \mu g/L$$

The HLCs are most accurate for those compounds with the higher concentrations in both the liquid and vapor phases—the lower molecular weight compounds in each of the Aroclor. Conversely, the calculated solubilities and vapor pressures are most accurate for those compounds that were present to a reasonable extent both in the air or water and in the starting Aroclors. These are the compounds of intermediate molecular weight in each of the Aroclors. Only small amounts of the higher molecular weight compounds in each Aroclor mixture dissolved or evaporated. Thus, the results obtained for these compounds are much less precise and probably less accurate. Also, the S°_L of the high molecular weight compounds could be increased by the presence of small amounts of surface layer contamination in the samples (see above).

The average molecular weight reported for the Aroclor mixtures was determined by dividing the weight of the Aroclor sample by the sum of the moles of each CB compound present.

The reproducibility of the sampling was shown to be quite good. For instance, the results from a set of four water samples collected over a period of several days are believed to be typical. A total of 10 packed-column GCs was run on these four samples. The variation in the total amount of PCBs present in the four samples was ±2.1%. The variation in the area of the largest peak in the spectra was ±3.0% and in the major PCB component in the Aroclor was ±2.2%. The variation in the area of five toxaphene vapor samples of 2 L each was ±15%.

Since only one solution was used for each of the Aroclor mixtures measured, the reliability and reproducibility of these preparations could not be checked. They could, however, be checked against one another. If the behavior of the individual CBC was close to ideal, the S°_L and P°_L data for each compound should be similiar, regardless of which mixture it was measured in. The correlations between the solubilities and vapor pressures for individual compounds present at more than 0.5 mol % in Aroclor 1242 and 1254 and in Aroclor 1254 and 1260 are shown by

$$S^{\circ}_{1260} = 0.77S^{\circ}_{1254} + 0.008 \qquad r = 0.995$$

$$P^{\circ}_{1260} = 0.69P^{\circ}_{1254} + 0.004 \qquad r = 0.998$$

$$S^{\circ}_{1254} = 1.32S^{\circ}_{1242} - 0.006 \qquad r = 0.86$$

$$P^{\circ}_{1254} = 1.15P^{\circ}_{1242} - 0.083 \qquad r = 0.925$$

The Aroclor 1242 spectra were run by a different laboratory. This may account for the greater scatter in the 1254 vs. 1242 correlation. The bias and variability in these correlations indicate that the reproducibility with this method is ±40% or less.

It is important to keep in mind that the data reported here for the solubility and volatility of the Aroclors refer only to the particular lots (FDA) used in the experiments. Because of their dominance in the water and vapor phases, small variations in the amounts of the lower molecular weight CB compounds in the mixtures can make significant differences in the total solubility and vapor pressure. For example, the Aroclor 1254 from the FDA had 17.5% of its mass in compounds with IUPAC no. <65. These compounds contributed about 53% of the mass of the PCBs in the vapor and solution phases. PCBs from a second lot contained only one-third the amount of the compounds with IUPAC no. <65. The calculated solubility and volatility of this PCB lot is 28% less than those of the FDA PCBs.

Results

Table I is a composite summary of the results from the 20 °C equilibrations of the Aroclors. The IUPAC number (*27*) for each of the compounds found is shown along with a descriptor showing the chlorine substitution pattern on each compound. The mole fraction of each individual CB compound in the different Aroclors used is shown. Also listed are the vapor pressures (P°_L), solubilities (S°_L), and HLCs of each of the pure CB compounds (as subcooled liquids), calculated from one or more of the Aroclor mixtures as was discussed above.

Even under optimum conditions of the capillary GC, not all of the individual CBC that were present in the mixtures could be completely resolved. In some cases the two compounds that eluted together were thought to be present in similar amounts. For these, the amount found was apportioned equally between the two compounds. They are indicated in Table I with a "&", and the two compounds in each such pair from each Aroclor will have the same calculated physical properties. In other cases most of the response is thought to be due to one compound of the pair. For these, the entire amount is assumed to be due to the major component, which is indicated with an "#" in Table I. The minor component of these pairs is indicated in the footnotes, but no calculations were made of its physical properties.

Summary data calculated and determined for the Aroclor and toxaphene mixtures by capillary GC are shown in Table II. Data determined by packed-column chromatography are also included for the Aroclors at 4 °C. The amounts shown were determined by summing all of the individual compounds quantified in the chromatograms. Considering the errors in sampling and analysis and in comparing the results with others, the errors associated with most of the results in Table II are probably on the order of ±50% or more. The HLC results may be more accurate because of the cancellation of some of the errors.

The 4 °C data are available only from packed-column GC analyses, and thus the results cannot be directly compared to the capillary GC results at 20 °C. Clearly, the large temperature effect on the vapor pressures is the principal cause of the temperature dependence of the HLCs.

The results for toxaphene are also shown in Table II. Since individual response factors are not available, only relative areas could be determined. For instance, the solubility in μg/L was calculated by determining the capillary GC area from a water sample saturated with toxaphene and dividing that area by the chromatographic area per microgram of a toxaphene standard. The solubility in mol/m^3 was calculated by assuming an average M_r of 350 for the toxaphene in solution. The HLC was just the ratio of the area of vapor sample per molar volume to the area of the water sample per cubic meter. It is independent of an assumed molecular weight. In addition, the toxaphene chromatograms were divided into five equal sections on the basis of relative GC retention time, and the HLC was determined on each section. The average was 7.0 with a standard deviation of ±3.5. There was no trend to the data, and the HLCs of four of the sections were quite close.

Discussion

The trends in the solubilities and vapor pressures of the individual compounds are surprisingly uneventful. The differences between individual compounds are not large; in fact, in many cases the differences are not statistically significant. A close look at the data, however, does show patterns indicating that the differences can be real. For instance, many of the compounds that have a relatively low HLC contain the 2,3 and 2,3,5 chlorine substitution pattern on one or both rings. Likewise, many of the compounds with high solubility and high vapor pressures contain the 2,3,6 chlorine substitution patterns.

Shown in Table III are comparisons between our reported solubilities for the subcooled liquids (S°_L) at 20 °C, the reported solubilities of solid CBC (S°_S) by Miller et al. (*4*) and Dickhut et al. (*6*) at the indicated temperature, the solubility of the solids corrected to that of the subcooled liquids with reported heats of melting (ΔH_m; ref 4), and the corrected solubility at 20 °C of the data of Miller et al. with enthalpies of solution (ΔH_{sn}; ref 6). The comparison looks reasonable. The agreement is within a factor of 2 for the results from those very different methods. There is perhaps some bias between the results. The poorest comparison is with compound 171, which is at the end of the range of our useful data and thus of low reliability. The variability between our results and the other results compared here is similar to those reported by Dickhut et al. (*6*) for different determinations of the solubilities of the solids by different laboratories.

Our only information on the temperature sensitivity of the solubility was obtained by using packed-column GC data (Table II). The changes found were small; in fact, the only change in solubility between 4 and 20 °C that is greater than the experimental errors is the factor of 1.46 for Aroclor 1242. The reason for the small change in solubility for Aroclor 1260 is not clear. While the solution was at 4 °C for several months before the measurements were made, it is possible that the solution was still supersaturated.

In contrast to these results, Dickhut et al. (*6*) found an average solubility difference of a factor of 2.55 between 4 and 20 °C for the three compounds they measured at these two temperatures. Besides experimental error and difference that might be found with compound-specific analysis, a reason for the difference between these values is that the measurements of Dickhut et al. (*6*) were made on the solid compounds. The enthalpies of solution will be lower for subcooled liquids, resulting in a smaller tem-

perature coefficient for the solubility and better agreement with out results. To use the data of Dickhut et al. (*6*) for modeling the fate of these compounds in the environment, their temperature coefficients should be corrected to what they would be for subcooled liquids.

Foreman and Bidleman (*8*) reported the vapor pressures determined with a gas chromatographic method and Aroclor mixtures, which gave vapor pressures of the individual CBC as subcooled liquids (P_L^0). A correlation of 54 of the individual compounds, from compound 4 to 153, gives

$$P_L^0(\text{this work}) = 0.835P_L^0(\text{ref 8}) + 3.5 \qquad r = 0.999$$

In addition, the average ratio of the P_L^0 for each compound determined in this study divided by that determined by Foreman and Bidleman (*8*) was 0.78 ($\sigma = 0.175$). Thus, the results from these two methods are in very good agreement, with some bias between them.

Of the parameters discussed, the HLC should be the one that different measurement and estimation techniques should give the closest results. This is because the HLC is a ratio and many experimental or theoretical sources of error should cancel. Burkhart et al. (*13*) recently presented an excellent discussion of the determination and estimation of HLCs for PCBs. They also predicted the HLCs for all 209 CBC and compared their results to previous measurements and estimates. A comparison of our results with their estimates is shown in Table IV. It can be seen that the agreement is very good. For the Aroclor mixtures themselves the differences are all less than 25%. This variation is less than that found between different lots of the Aroclors (see above).

Our data show a definite trend toward lower HLCs with increasing molecular weight. This can be seen in the data in Table I. The plot of the 209 HLCs of Burkhart et al. (*13*) does not show such a trend. There is also less variability between the HLCs of any particular set of HLC isomers in our data than was found by Burkhart et al. (*13*). The fact that the Aroclors do not contain all the possible compounds and the compounds are present in different amounts in the mixtures could explain some of the differences.

Since they are based on the subcooled CB mixtures, the data in Table I can be used to do a great variety of partitioning calculations on PCB mixtures. For instance, if the molar composition of PCBs in a sediment sample is known, the composition of the dissolved and vapor phases in equilibrium with the sediments can be readily calculated.

The transfer of volatile compounds across the air/water interface has been modeled (*28*) by the two-film resistance model of Whitman (*29*). In this model, the resistance to transfer ($1/K_{OL}$) of a compound through the air/water interface is treated as the sum of the resistances to transfer in the liquid and gas films (K_L and K_G) adjacent to the air/water interface:

$$\frac{1}{K_{OL}} = \frac{1}{K_L} + \frac{RT}{HK_G} \qquad (3)$$

Mackay et al. (*30*) have estimated the liquid and gas mass-transfer coefficients for PCB-type compounds to be 0.04 and 15 m/h, respectively. Using these coefficients and eq 3, it can be calculated that the resistance to transfer of compounds with an HLC greater than 7×10^{-4} will be more than 90% in the liquid phase, and the gas-phase transfer coefficient may be neglected (see Figure 1). Likewise, the resistance to transfer of compounds with HLC less than 7×10^{-6} will be more than 90% in the gas phase, and the liquid-phase transfer coefficient may be neglected. The transfer rates (K_{OL}) across the air/water interface will be smaller for the compounds with the lower HLCs (high molecular weight compounds; gas-phase control). The net transfer for all of the compounds, of course, will be in the direction to equalize the fugacities. The flux of a compound may be estimated if the difference in the fugacity of the compound in the vapor and liquid phases is known. The flux is the K_{OL} times the difference in fugacity.

Unfortunately, the data in Tables I and II indicate that, consistent with their perverse nature, the PCBs are neither solely gas phase nor liquid phase controlled at either 20 or at 4 °C. Thus, this property of the PCBs falls into the midrange where both transfer resistances have to be considered. Since the term containing the gas transfer rate coefficient also includes the very temperature-sensitive HLC, the K_{OL} for each compound will also vary with the temperature.

Toxaphene, on the other hand, should be more than 90% gas phase controlled and should have lower mass-transfer rates at all temperatures. Unlike the PCBs, it should be efficiently scrubbed from the air by partitioning into rain.

At this time, Lake Michigan seems to provide a useful illustration of the implications of these results. Doskey and Andren (*31*) have reported that the concentration of PCBs in the atmosphere in mid Lake Michigan is about 0.9 ng/m^3, and Rice et al. (*32*) have reported the concentration of PCBs in the open lake waters, which pass through a 0.45-μm filter, to be about 4 ng/L. A value of 1 ng/m^3 of PCBs (M_r 240; Arclor 1242) in the vapor phase is equivalent to a fugacity of 1×10^{-13} atm at 20 °C. With an HLC = 1.9×10^{-4} atm-m^3/ml, 4 ng/L in the liquid phase is equivalent to 1.4×10^{-6} mol/m^3 or a fugacity of 27×10^{-13} atm. Thus, the direction of transfer seems to be clearly from the water to the atmosphere at 20 °C as the water fugacity would support a vapor concentration of ~30 ng/m^3.

At 4 °C, with an HLC = 0.2×10^{-4} atm-m^3/mol, 4 ng/L of dissolved PCBs has a fugacity of 43×10^{-14} atm, and 1 ng/m^3 of PCB vapor has a fugacity of 9×10^{-14} atm. Thus even at 4 °C, the direction of transfer still seems to be from the water to the atmosphere. These data support the conclusion that the atmosphere, rather than the sediments, is the major sink for PCBs in Lake Michigan (*2, 3, 18*) and for other organics with HLCs in this range in this and other bodies of water.

The results on the solubility of organic mixtures found here have implications in the design and interpretation of aquatic toxicology studies. Aqueous solutions of PCBs (and other mixtures of organics) used in toxicology studies are almost always prepared by adding a solution of PCBs in acetone (or methanol or other water-soluble organic) to the water sample be used in the test. However, when investigators calculate the percent saturation, with its implications to fugacity and toxicity, they always refer to the reported "solubility" of PCBs (~56 μg/L; ref 23), determined by equilibrium partitioning, in a manner similar to that used in our studies (method 1). The decreased solubility of these compounds in saline waters also needs to be taken into account (*14*).

Solutions prepared, as above, by adding a solution of PCBs to water (method 2) will have a different composition and fugacity than if prepared by equilibrium partitioning. The fact that the composition is different is obvious. In method 1 you are partitioning, and more of the more soluble compounds will dissolve. In method 2, all of the added material is dissolving, and thus the starting mixture

Table I. Physical Properties of Individual Chlorobiphenyl Compounds at 20 °C[a]

B&Z no.	Cl (X) and H (O) substitution pattern		M_r	mole fraction × 1000 in standard 1242	1254	1260	S, μg/L	P, atm × 10^9	HLC, atm·m³/mol × 10^4
4[b]	XOOOO	XOOOO	223.1	62.4	0.0	0.0	1124.00	1502.94	2.98
6	XOOOO	OXOOO	223.1	14.6	0.0	0.0	579.83	788.82	3.04
7	XOXOO	OOOOO	223.1	5.9	0.0	0.0	612.93	986.99	3.59
8[b]	XOOOO	OOXOO	223.1	145.3	0.0	0.0	538.29	676.47	2.80
16	XXOOO	XOOOO	257.6	69.1	3.4	0.0	293.04	271.62	2.38
17	XOXOO	XOOOO	257.6	38.0	4.3	0.0	259.19	330.81	3.26
18	XOOXO	XOOOO	257.6	85.7	8.0	0.0	298.63	347.44	2.99
19	XOOOX	XOOOO	257.6	13.9	3.4	0.0	448.33	521.95	3.03
22	XXOOO	OOXOO	257.6	14.9	1.0	0.0	141.65	109.58	1.99
24	XXOOX	OOOOO	257.6	6.5	0.7	0.0	132.01	164.23	3.17
25	XOXOX	OXOOO	257.6	0.0	1.3	0.0	20.45	32.09	4.04
26	XOOXO	OXOOO	257.6	13.7	2.3	0.0	138.41	180.46	3.39
27	XOOOX	OXOOO	257.6	0.0	1.0	0.0	38.58	42.03	2.81
28[b]	XOXOO	OOXOO	257.6	50.9	2.0	0.0	143.16	147.24	2.64
31[b]	XOOXO	OOXOO	257.6	50.9	2.0	0.0	143.16	147.24	2.64
33	OXXOO	XOOOO	257.6	54.6	8.2	0.0	132.55	117.14	2.24
37	OXXOO	OOXOO	257.6	30.6	4.2	0.0	71.89	44.77	1.52
40	XXOOO	XXOOO	292.0	9.2	4.2	0.0	80.70	44.64	1.61
41[b]	XXXOO	XOOOO	292.0	37.4	10.8	0.0	64.80	45.31	2.01
42	XXOOO	XOXOO	292.0	0.0	3.7	0.0	60.83	41.39	1.99
44	XXOOO	XOOXO	292.0	39.0	27.8	0.0	100.05	63.14	1.89
46	XXOOO	XOOOX	292.0	3.7	2.0	0.0	105.93	89.35	2.57
48	XOXXO	XOOOO	292.0	0.0	6.2	0.0	29.95	26.16	2.55
49	XOXOO	XOOXO	292.0	22.6	14.5	0.0	78.14	73.26	2.76
52[b]	XOOXO	XOOXO	292.0	27.9	56.2	0.0	112.57	89.19	2.38
53	XOOXO	XOOOX	292.0	0.0	3.4	0.0	108.54	105.22	2.83
56[b]	XXOOO	OXXOO	292.0	20.6	4.8	0.0	38.94	21.43	1.62
60[b]	XXXOO	OOXOO	292.0	20.6	4.8	0.0	38.93	21.43	1.62
63	XXOXO	OOXOO	292.0	0.0	1.1	0.0	26.27	26.01	2.89
64	XXOOX	OOXOO	292.0	0.0	8.4	0.0	93.65	54.39	1.70
66	XOXOO	OXXOO	292.0	52.4	24.5	0.0	36.76	24.83	2.01
70[b]	XOOXO	OXXOO	292.0	25.8	0.0	0.0	36.18	23.29	1.88
74	XOXXO	OOXOO	292.0	18.0	9.7	0.0	30.64	20.93	2.09
76[b]	OXXXO	XOOOO	292.0	25.8	27.1	0.2	55.13	24.07	1.28
81[b]	OXXXO	OOXOO	292.0	0.0	0.0	0.2	0.00	0.00	0.00
82	XXXOO	XXOOO	326.4	2.0	9.7	0.0	29.08	10.42	1.17
83	XXOXO	XXOOO	326.4	0.0	4.5	0.3	28.23	15.18	1.64
84	XXOOX	XXOOO	326.4	0.0	36.4	0.0	47.02	25.05	1.74
85	XXXOO	XOXOO	326.4	2.9	15.9	0.0	21.91	11.04	1.65
87	XXXOO	XOOXO	326.4	0.0	33.2	3.8	29.41	11.47	1.27
91	XXOOX	XOXOO	326.4	0.0	11.3	0.0	39.45	32.77	2.71
95[b]	XXOOX	XOOXO	326.4	0.0	69.7	28.8	54.13	33.05	1.98
97	XOXXO	XXOOO	326.4	0.0	18.3	1.1	28.41	12.92	1.49
99	XOXXO	XOXOO	326.4	0.0	17.0	0.0	22.19	14.54	2.14
101	XOXXO	XOOXO	326.4	0.0	60.5	25.7	26.26	14.43	1.79
107	XXOXO	OXXOO	326.4	0.0	3.5	0.0	14.84	2.58	0.57
110	XXOOX	OXXOO	326.4	6.5	84.9	14.6	28.82	9.36	1.06
114	XXXXO	OOXOO	326.4	0.0	1.8	0.0	15.98	3.40	0.69
118	XOXXO	OXXOO	326.4	0.0	52.4	3.8	13.44	3.50	0.85
122	OXXXO	XXOOO	326.4	0.0	1.8	1.1	12.84	3.17	0.60
124	OXXXO	XOOXO	326.4	0.0	2.8	0.0	15.81	2.57	0.53
128	XXXOO	XXXOO	360.9	0.0	10.7	4.0	6.70	0.97	0.57
129	XXXXO	XXOOO	360.9	0.0	4.4	0.0	11.71	0.00	0.00
130	XXXOO	XXOXO	360.9	0.0	4.2	0.5	5.69	1.59	1.07
131	XXXOX	XXOOO	360.9	0.0	1.2	0.6	12.12	2.60	0.65
134	XXOXX	XXOOO	360.9	0.0	3.4	3.6	12.95	3.53	0.97
135[b]	XXOXO	XXOOX	360.9	0.0	3.3	8.5	12.94	5.00	1.40
136	XXOOX	XXOOX	360.9	0.0	7.6	16.9	20.16	12.58	2.25
137	XXXXO	XOXOO	360.9	0.0	3.0	1.7	8.40	1.48	0.68
138	XXXOO	XOXXO	360.9	0.0	49.2	65.3	7.29	1.45	0.75
141	XXXXO	XOOXO	360.9	0.0	8.3	29.2	7.55	2.02	0.97
144[b]	XXXOX	XOOXO	360.9	0.0	3.3	8.5	12.94	5.00	1.40
145[c]	XXXOX	XOOOX	360.9	0.0	0.0	0.2	0.00	0.00	0.00
146	XXOXO	XOXXO	360.9	0.0	6.6	12.3	7.59	1.85	0.88
149	XXOOX	XOXXO	360.9	0.0	33.6	78.6	12.17	4.90	1.48
151	XXOXX	XOOXO	360.9	0.0	6.2	29.4	13.55	5.89	1.57
153	XOXXO	XOXXO	360.9	0.0	62.4	114.4	9.14	2.50	0.99
156	XXXX	OXXOO	360.9	0.0	6.0	3.9	5.33	0.00	0.00
158	XXXOX	OXXOO	360.9	0.0	7.6	7.4	8.07	0.96	0.43
167	XOXXO	OXXXO	360.9	0.0	1.8	0.0	0.00	0.00	0.00
170[b]	XXXXO	XXXOO	395.3	0.0	9.0	74.5	3.47	0.13	0.15
171	XXXOX	XXXOO	395.3	0.0	2.1	15.1	4.12	0.00	0.00
172	XXXXO	XXOXO	395.3	0.0	0.9	8.4	4.30	0.00	0.00
173	XXXXX	XXOOO	395.3	0.0	0.0	0.8	4.16	0.00	0.00

Table I (Continued)

B&Z no.	Cl (X) and H (O) substitution pattern		M_r	mole fraction × 1000 in standard 1242	1254	1260	S, μg/L	P, atm × 10^5	HLC, atm·m³/mol × 10^5
174	XXXXO	XXOOX	395.3	0.0	3.9	57.0	5.25	0.65	0.49
175	XXXOX	XXOXO	395.3	0.0	0.0	5.4	8.94	0.00	0.00
176	XXXOX	XXOOX	395.3	0.0	0.4	4.0	5.85	1.33	0.90
177	XXOXX	XXXOO	395.3	0.0	2.0	23.2	4.82	0.41	0.33
178	XXOXX	XXOXO	395.3	0.0	1.1	13.2	8.84	1.45	0.65
180	XXXXO	XOXXO	395.3	0.0	7.1	94.9	3.85	0.31	0.32
183	XXXOX	XOXXO	395.3	0.0	2.3	24.0	4.90	0.85	0.68
185	XXXXX	XOOXO	395.3	0.0	2.7	6.5	5.46	0.00	0.00
187[#]	XXOXX	XOXXO	395.3	0.0	2.7	51.9	4.51	0.93	0.82
189	XXXXO	OXXXO	395.3	0.0	0.0	1.4	0.00	0 00	0.00
191	XXXOX	OXXXO	395.3	0.0	0.2	1.2	0.00	0.00	0.00
193	XXOXX	OXXXO	395.3	0.0	0.5	5.2	0.00	0.00	0.00
194	XXXXO	XXXXO	429.8	0.0	0.4	16.5	0.00	0.00	0.00
195[#]	XXXXX	XXXOO	429.8	0.0	1.1	33.0	0.00	0.00	0.00
198	XXXXX	XXOXO	429.8	0.0	0.2	2.3	0.00	0.00	0.00
201	XXOXX	XXXXO	429.8	0.0	0.0	33.4	0.00	0.00	0.00
203	XXXXX	XOXXO	429.8	0.0	1.0	36.8	0.00	0.00	0.00
205	XXXXX	OXXXO	429.8	0.0	0.0	1.0	0.00	0.00	0.00
206	XXXXX	XXXXO	464.2	0.0	0.0	6.9	0.00	0.00	0.00
207	XXXXX	XXXOX	464.2	0.0	0.0	1.1	0.00	0.00	0.00

[a] The solubilities, vapor pressures, and HLCs were calculated from the results of the equilibrium experiments as described in the text. Compounds indicated with (#) were not completely resolved from small amounts of other chlorobiphenyl compounds. Compounds indicated with (&) are compounds that eluted together in similar amounts, see text.

Table II. Properties of Aroclor and Toxaphene Mixtures Studied

	Aroclor 1242		Aroclor 1254		Aroclor 1260		toxaphene, 20 °C
	4 °C[a]	20 °C	4 °C[a]	20 °C	4 °C[a]	20 °C	
solubility, mol/m³ × 10^6		1160		150		48.5	5600[d]
solubility, μg/L	190	277	39	43	14	14.4	550
vapor pressure, atm × 10^5		329		29		8.3	8.8[d]
vapor pressure, μg/m³	310	3250	49	337	15	92	140
HLC, atm·m³/mol × 10^4	0.37	2.8	0.28	1.9	0.25	1.7	0.06
av M_r							
standard mixture[b]		262		327		380	414[e]
solution phase[c]		238		285		296	350[e]
vapor phase[c]		237		280		265	350[e]

[a] Packed-column GC data. [b] FDA standard PCB mixtures used to make measurements. [c] Phases in equilibrium with a large amount of the FDA standard PCB mixture. [d] Calculated using estimated molecular weights. [e] Estimates only (M_r of $C_{10}H_{10}Cl_8$ 414).

Table III. Comparison of Reported Solubility of Chlorobiphenyl Compounds

CB compd IUPAC no.	$S^0_{L,25}$, μg/L[a]	$S^0_{L,25}$, μg/L[b]	$S^0_{L,25}$, μg/L[c]	$S^0_{L,25}$, μg/L[d]	$S^0_{L,25}$, μg/L[e]
49	16.4	51.5			78
101	19.3	59.6	53.3	42.5	26
128	0.28	9.6			7
136	6.0	41.3	34.4	25.8	20
171	2.2	16.2			4

[a] Measured value (4). [b] Calculated from $S^0_{L,25}$ (4) using ΔH_m (4). [c] Calculated from $S^0_{L,25}$ (4) using ΔH_m (4) and ΔH_m (6). [d] Measured value (6). [e] Measured value, this work.

Table IV. Comparison of Reported HLCs for Aroclor Mixtures

Aroclor mixture	HLC, atm·m³/mol, 20 °C: Burkhart et al. (13)	this work
1242	2.27×10^{-4}	2.8×10^{-4}
1254	1.8×10^{-4}	1.9×10^{-4}
1260	2.1×10^{-4}	1.7×10^{-4}

and the solution have the same composition.

A solution saturated with PCBs by method 2 will have a smaller amount of chlorinated biphenyl compounds in solution because the least soluble compounds will be come saturated well before the most soluble compounds. The solubility of a PCB mixture in water prepared by method 2 can be readily calculated from the data from Table I. Consider adding an acetone solution of Aroclor 1254 to water. As long as all the PCBs dissolve, the composition of the water phase is the same as the Aroclor 1254. However, as soon as one of the CBC becomes saturated, a second phase, an insoluble PCB phase, will separate. Since it is in equilibrium with the PCBs in the water phase whose composition is known, the relative composition of the PCB phase can be calculated by using the S^0_L values from Table I. This composition is then normalized (sum of the mole fractions of the components equals 1) and its solubility calculated with the S^0 values. The results obtained by doing these calculations for Aroclor 1242, 1254, and 1260 are shown in Table V. It can be seen that the solubility of Aroclors with method 2 is only about one-third the reported "solubility" of these Aroclors (determined by method 1).

The different composition and solubilities of Aroclor solutions, prepared by these different methods, need to be taking into account in designing and interpreting aqueous studies using the Aroclors. More care needs to be taken to prevent formation of an undissolved PCB phase for studies done at high concentrations (33-37). The

Table V. Composition of Saturated Water Phases As Determined (Method 1) or Calculated (Method 2)[a]

	PCB mole fraction		water phase, μg/L	
	method 1	method 2	method 1	method 2
		Aroclor 1242		
Cl = 1	0.000	0.000	0.00	0.00
Cl = 2	0.228	0.028	160.40	17.78
Cl = 3	0.429	0.213	96.91	38.59
Cl = 4	0.331	0.709	19.21	33.81
Cl = 5	0.012	0.050	0.35	1.31
Cl = 6	0.000	0.000	0.00	0.00
Cl = 7	0.000	0.000	0.00	0.00
Cl = 8	0.000	0.000	0.00	0.00
Cl = 9	0.000	0.000	0.00	0.00
sum			276.88	91.49
		Aroclor 1254		
Cl = 1	0.000	0.000	2.42	0.00
Cl = 2	0.000	0.000	4.09	0.00
Cl = 3	0.042	0.013	2.73	0.59
Cl = 4	0.214	0.052	17.96	3.46
Cl = 5	0.426	0.285	13.86	7.69
Cl = 6	0.223	0.547	2.04	4.41
Cl = 7	0.016	0.104	0.08	0.34
Cl = 8	0.000	0.000	0.00	0.00
Cl = 9	0.000	0.000	0.00	0.00
sum			43.18	16.50
		Aroclor 1260		
Cl = 1	0.000	0.000	0.96	0.00
Cl = 2	0.000	0.000	2.45	0.00
Cl = 3	0.002	0.000	1.40	0.01
Cl = 4	0.011	0.001	0.69	0.04
Cl = 5	0.079	0.012	2.66	0.32
Cl = 6	0.385	0.180	3.97	1.72
Cl = 7	0.387	0.442	1.74	1.90
Cl = 8	0.127	0.340	0.45	0.68
Cl = 9	0.008	0.025	0.02	0.05
sum			14.34	4.71

[a] Starting PCB composition for both water phases shown in column 1. Composition of PCBs in equilibrium with the method 2 water phase shown in column 2. Compositions listed by number of chlorines per molecule.

different toxicities of PCB solution prepared by these two methods need to be taken into account in interpreting the results (33). Since PCBs invariably get into natural water systems by partitioning from a nonpolar phase, it would seem to be more appropriate to prepare test solutions by method 1.

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Registry No. Aroclor 1242, 53469-21-9; Aroclor 1254, 11097-69-1; Aroclor 1260, 11096-82-5; toxaphene, 8001-35-2.

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